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MATERIALS REPORT 115

THE EFFECT OF SOME WATER-DISPLACING CORROSION PREVENTIVES ON CORROSION OF ALUMINIUM ALLOYS 7075-T651 AND 2024-T6

by

L. WILSON and R. S. G. DEVEREUX

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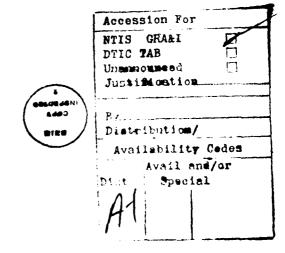
SUMMARY

The effectiveness of six commercial water-displacing corrosion preventive formulations (WDCP's) in inhibiting corrosion of two aluminium alloys used in aircraft construction has been investigated. Two solutions, 0·1 molar sodium chloride and 0·1 molar sodium chloride-0·18 molar aluminium chloride, were chosen to simulate aircraft service environments in the laboratory tests. Testing was done by treating specimens with WCDP's prior to exposure to the corrosive media and also by immersing specimens in the test media and then adding WDCP's to these solutions. Evaluation was by weight loss measurements and subsequent microscopic examination. In some of the tests, a novel method of estimating weight loss (during the course of a test) by analysis of small samples of solution was used. All six WDCP's tested were found to inhibit corrosion of the aluminium alloys significantly under the test conditions.



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1. INTRODUCTION

At the request of the RAAF and RAN, ARL is currently investigating methods of preventing and controlling corrosion of aircraft structures. One such method, used by aircraft manufacturers and operators throughout the world, involves the application of water-displacing corrosion preventive formulations (WDCP's) to areas of the aircraft where corrosive fluids tend to accumulate. When aircraft operate in a marine environment, a salt solution produced from sea spray and condensed atmospheric moisture may collect on areas such as fuselage and wing skins resulting in surface corrosion. The potentially more serious crevice corrosion may result from penetration of the solution into crevices formed at lap joints, fastener holes and other faying surfaces.

WDCP's usually consist of a film former dissolved in a mixture of a volatile water-displacing compound and a low-surface-tension carrier solvent together with a non-volatile hydrophobic additive and a corrosion inhibitor. They act by firstly penetrating into crevices and then displacing moisture from surfaces. Evaporation of the water-displacing compound and the carrier solvent then leaves a waterproof residue on the surfaces, which consists of the film former, the hydrophobic additive and the corrosion inhibitor. The nature of this residue varies with different WDCP's which can be classified according to the three common types of residue, viz.

- (1) Oily film
- (2) Soft or grease-like film
- (3) Hard resin-like film.

Many WDCP's have been approved as meeting the requirements of various national military specifications. However, none of these specifications prescribes tests for assessing the effectiveness of WDCP's in preventing or controlling the corrosion of aluminium alloys. An earlier report (1) showed that each of six WDCP's tested, including at least one of each of the abovementioned types, had an inhibiting effect on stress-corrosion cracking in 7075-T651 aluminium alloy. This report describes laboratory tests carried out to determine the effectiveness of the same six WDCP's in controlling surface corrosion and crevice corrosion of aluminium alloys of the types used in aircraft operating in a marine environment. The six WDCP's are listed, together with their relevant specifications and characteristic type, in Table 1.

TABLE 1

Trade Name	Relevant Specification	Туре
Ardrox 3961	DEF. STAN. 68/10-PX24	Oily film
Mobilarma	DEF. AUST. 1002—PX112	Oily film
Amiguard	MIL-C-85054-AS	Hard film
Boeshield T9	BMS-3-23	Soft film
Tectyl 472 B	MIL-C-23411 A(YD) Type 2	Oily film
WD 40	DEF. STAN. 68/10-PX24	Oily film

2. EXPERIMENTAL

2.1 Choice of corrosive environment

0.1 Molar (0.1 M) sodium chloride solution was chosen to represent the environment found on the external surfaces of aircraft operating in a marine atmosphere. Experiments conducted by the authors have confirmed reports by other investigators (2) that the solutions found within cracks and crevices in aluminium alloys exposed to 0.1 M sodium chloride solutions have a pH of approximately 3.5 and contain aluminium chloride in solution. Accordingly, an aluminium chloride/sodium chloride solution with a pH of 3.5 was used to simulate the environment in cracks and crevices in the structure of aircraft operating in a marine atmosphere. This solution was 0.18 M with respect to aluminium chloride and 0.1 M with respect to sodium chloride. The aluminium chloride solution was made by dissolving super-pure aluminium in the appropriate quantity of concentrated hydrochloric acid.

2.2 Choice of alloys for testing

Since airframe surfaces, such as fuselage and wing skins, are often fabricated from 2024-T6 aluminium alloy, and primary structural components are often made from 7075-T651 aluminium alloy, specimens of both these alloys were used in the corrosion tests. 2024-T6 aluminium alloy specimens were tested only in the 0·1 M sodium chloride solution because this solution resembles most closely the environment found on airframe surfaces in fuselage bilges and on wing skins, etc. 7075-T651 aluminium alloy specimens were tested in both the 0·1 M sodium chloride solution and the 0·18 M aluminium chloride-0·1 M sodium chloride solution because primary structural components may be subjected to both simple condensate environments and, where joints, fasteners or other faving surfaces are involved, to the more acid environment of crevice solutions.

All test specimens were square prisms, $(20 \times 6 \times 6 \text{ millimetres})$, having a surface area of 550 square millimetres, abraded to a 600-grit finish, degreased, and weighed.

2.3 Corrosion tests

The circumstances applying to the use of WDCP's during assembly of an aircraft differ from those applying after the aircraft becomes operational. When WDCP's are applied during assembly, the volatile constituents of the WDCP evaporate leaving the waterproof film. Those applied ing service are often used as a stop-gap measure between overhauls, and consequently may be applied to surfaces already wet with condensate. As several litres of condensate may collect in an aircraft after one flight, the WDCP may be required to inhibit corrosion in the presence of relatively large quantities of aggressive fluids. Two series of corrosion tests were therefore devised to assess the relative effectiveness of the WDCP's in preventing corrosion in conditions roughly approximating (a) those applying at the manufacturing stage, and (b) those applying once the aircraft has been in service.

In series (a), the specimen was immersed in the WDCP for 30 seconds and left to dry in laboratory air for three days. (Previous experiments at ARL have shown that up to three days is required for the volatile constituents of WDCP's to evaporate). The specimen was then suspended by a nylon thread in 100 ml of test solution in a stoppered glass bottle. The bottle was shaken for ten seconds every working day of the test period. Micro samples of the test solution were periodically analysed for magnesium using atomic absorption spectroscopy and, from the results, the weight loss of the specimen was calculated; this technique will be described in detail elsewhere. At the end of the test the specimen was taken from the bottle, the WDCP residue removed and the specimen cleaned according to ASTM-G1-72. It was then weighed and examined using a low-power microscope.

In series (b), the specimen was suspended by a nylon thread in 90 ml of a test solution containing quantities of sodium chloride and aluminium chloride such that, on the addition of 10 ml of a WDCP, the resultant solution would be (i) 0.1 M NaCl, or (ii) 0.1 M NaCl-0.18 M AlCl₂. This series of tests was also carried out in a stoppered glass bottle and, after addition of the 10 ml of the WDCP, the bottle was shaken vigorously for 30 seconds. Because the water insoluble portion of the WDCP's floated on top of the test solutions and tended to cause blockages in the nebulization system of the atomic absorption spectrophotometer, it was

impracticable to monitor progressively the weight loss of these specimens. The bottle was shaken for thirty seconds each working day for the test period and, at the end of this time, the specimen was removed from the bottle, cleaned as before, weighed, and examined with the aid of a low-powered microscope.

3. RESULTS

(a) Specimens pretreated with WDCP's

Figures 1-3 and Tables 2 and 3 show that each of the WDCP's used as a pretreatment reduced the corrosion rate of both alloys. (It can be seen that the calculated weight losses from the atomic absorption analysis technique agree well with the weight losses determined at the end of the test). For both alloys in the 0·1 M sodium chloride solution, the least effective WDCP was Mobilarma. Figures 1 and 2 show that the relatively faster rate of corrosion of the specimens pretreated with Mobilarma is apparent from the first day of testing and increases quite rapidly after ten days. However, microscopic examination of the specimens which had been treated with Mobilarma revealed only general surface corrosion. This was also the case with the specimens which had been treated with Tectyl 472B. Those specimens which had been treated with WD40, Boeshield or Amlguard showed very slight pitting as well as light surface-staining. The control specimens were extensively pitted and had suffered severe surface corrosion. Ardrox 3961 afforded complete protection to the specimens on which it was used and no signs of either pitting corrosion or surface corrosion were apparent.

Table 3 and Figure 3 show that corrosion of aluminium alloy 7075-T651 specimens is much more severe in $0.1 \, \mathrm{M}$ sodium chloride- $0.18 \, \mathrm{M}$ aluminium chloride solution than in $0.1 \, \mathrm{M}$ sodium chloride solutions. Again, pretreatment of the specimens with a WDCP significantly reduced the rate of corrosion. WD40, Ardrox 3961, and Boeshield T9 were the most successful corrosion inhibitors in this environment. Mobilarma, Tectyl 472B, and Amlguard tended to lose their effectiveness fairly quickly.

Microscopic examination of the specimens tested in the sodium chloride-aluminium chloride test solution revealed that all specimens had suffered pitting corrosion and surface corrosion. In accordance with the weight-loss results, those specimens pretreated with WD40, Ardrox 3961, or Boeshield T9 were not as badly affected as the others.

(b) Specimens tested in solutions to which WDCP's were added

Table 4 shows that, in the second series of tests, each of the WDCP's inhibited corrosion of the specimens by the 0·1 M sodium chloride solution. This result was confirmed by micro-

TABLE 2

Measured weight loss after 23 days immersion in 0·1 Molar Sodium

Chloride of control specimens and specimens pretreated with a WDCP

WDCP	Measured weight loss in grams per millimetre ²		
WDCP	7075-T651 Specimens	2024-T6 Specimens	
Nil	1·15×10 ⁻⁵	1·35×10 ⁻⁵	
Mobilarma	0.34	0.36	
Amlguard	0.10	0.05	
Boeshield T9	0.09	0.05	
WD 40	0.05	0.04	
Ardrox 3961	0.05	Nil	
Tectyl 472 B	0.04	0.05	

TABLE 3

Measured weight loss after 23 days immersion in 0·1 Molar Sodium Chloride-0·18 Molar Aluminium Chloride solution of control specimen and specimens pretreated with a WDCP

WDCP	Measured weight loss in grams per millimetre ² of 7075-T651 Specimens
Nil	8·71×10 ⁻⁵
Tectyl 472 B	4.33
Mobilarma	2 · 29
Amlguard	2.18
Boeshield T9	0.29
Ardrox 3961	0.24
WD 40	0.07

TABLE 4

Measured weight loss of specimens after 42 days immersion in 0·1 Molar sodium chloride solution containing 10 percent WDCP

WEGE	Measured weight loss in grams per millimetre		
WDCP	7075-T651 Specimens	2024-T6 Specimens	
Nil	1·93×10 ⁻⁵	2·58×10 ⁻⁵	
Mobilarma	0.10	0.09	
Amlguard	Nil	0.02	
Boeshield T9	Nil	0.04	
WD 40	Nil	0.11	
Ardrox 3961	Nil	0.13	
Tectyl 472 B	Nil	0.07	

TABLE 5

Measured weight loss of specimens after 42 days immersion in 0·1 Molar Sodium Chloride-0·18 Molar Aluminium Chloride solution containing 10 percent WDCP

WDCP	Weight loss in grams per millimetre ² of 7075-T651 Specimens		
Nil	19·4×10 ⁻⁵		
Amlguard	4.71		
WD 40	3.00		
Ardrox 3961	2 · 27		
Mobilarma	1 · 42		
Boeshield T9	0.09		
Tectyl 472 B	Nil		

scopic examination of the specimens at the completion of the test period, i.e. only the control specimens were pitted and showed signs of general surface corrosion. However, as indicated by the results in Table 5, those specimens tested in the 0·1 M sodium chloride-0·18 M aluminium chloride suffered various degrees of corrosion. Microscopic examination of the specimens showed the severity of pitting and general corrosion to be directly related to the weight-loss figures, e.g. while the control specimen was by far the most severely affected, the solution containing Amlguard produced a blackening of the surface of the specimen and large, deep pits on all surfaces. Specimens in solutions containing Boeshield T9 or Tectyl 472 B were very little affected.

4. DISCUSSION

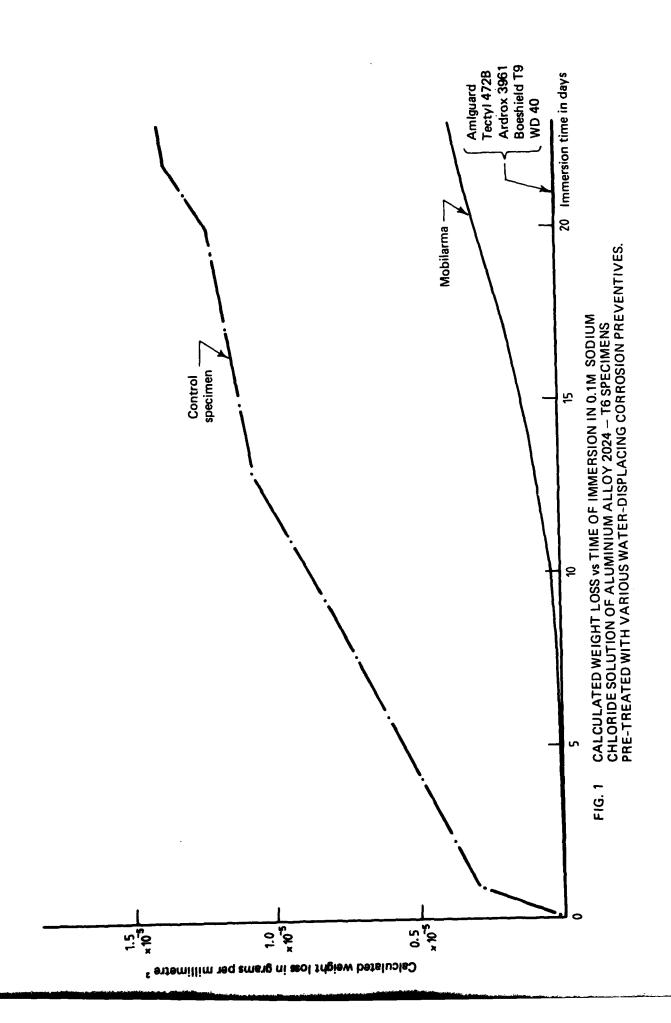
It is apparent that, in sodium chloride solution, all the WDCP's tested are almost completely effective corrosion inhibitors whether applied to the specimen before immersing it in the test solution or whether they are added to the test solution after the specimen is immersed. In the sodium chloride-aluminium chloride test solution, although they are still effective corrosion inhibitors, individual WDCP's vary in their degree of effectiveness in the two test situations, e.g. Tectyt 472 B is almost completely effective when added to the test environment but is the least effective of the six WDCP's tested when applied directly to the specimen before immersion. WD40, however, is the most effective of the six WDCP's tested when used as a thin film on the specimen before immersion and is relatively much less effective when added to the test solutions. It is postulated by the authors that the corrosion-inhibiting properties of the WDCP's when used as thin films deposited on clean surfaces and exposed to the test solutions arises from the hydrophobic nature of the deposited films, while their effectiveness when added to the test solution is due to the leaching into the solution of inhibitors present in the various formulations.

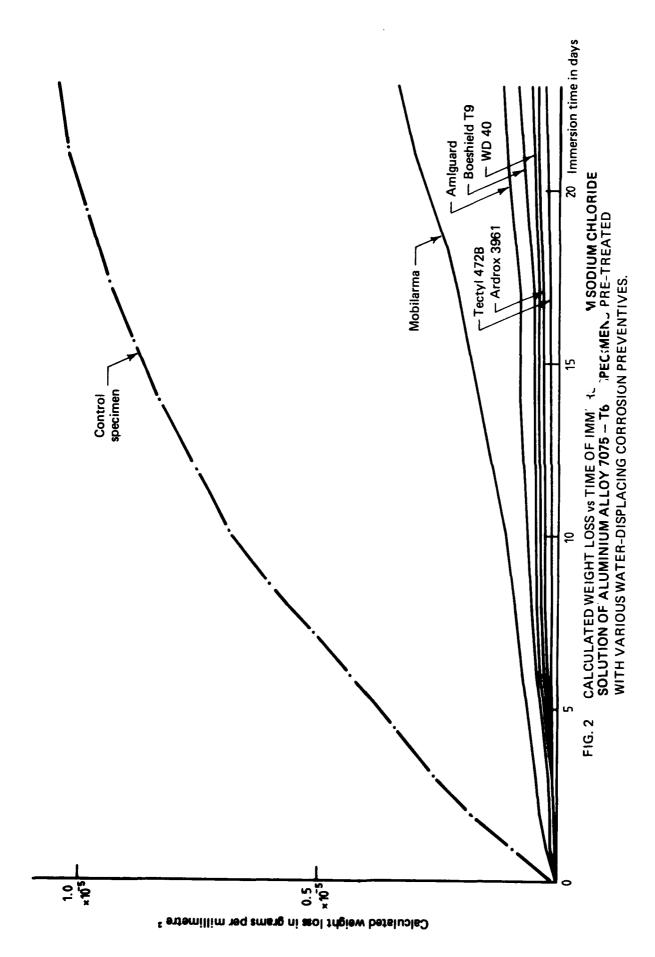
5. CONCLUSIONS

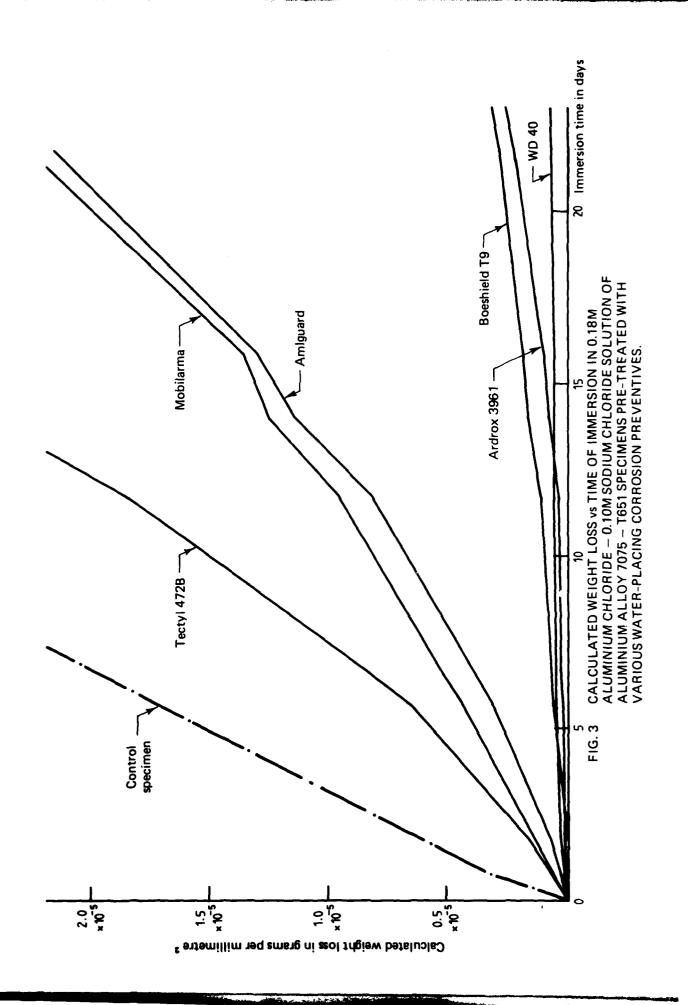
- 1. All WDCP's tested inhibited corrosion of 2024-T6 and 7075-T651 aluminium alloys under the test conditions.
- 2. Individual WDCP's varied in their effectiveness depending on the corrosive medium and on whether or not the corrosive solution was already present when they were applied.
- 3. Of the WDCP's tested, Boeshield T9 was the most consistently effective under all the test conditions described in this report. (Boeshield T9 has previously been found to be the most effective stress-corrosion inhibitor under laboratory test conditions (1)).

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- (1) L. Wilson and R. S. G. Devereux
- The effect of water-displacing corrosion preventives on stress-corrosion cracking of aluminium alloy 7076-T651. Dept. of Defence, ARL Mat. Note 132, March 1982.
- (2) M. Marek, J. Rinker and R. Hockman
- Solution chemistry in crevices and stress-corrosion cracks. Proc. 6th Int. Congress on Metallic Corrosion. Sydney, December 1975.







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16. Abstract				

The effectiveness of six commercial water-displacing corrosion preventive formulations (WDCP's) in inhibiting corrosion of two aluminium alloys used in aircraft construction has been investigated. Two solutions, $0 \cdot 1$ molar sodium chloride and $0 \cdot 1$ molar sodium chloride- $0 \cdot 18$ molar aluminium chloride, were chosen to simulate aircraft service environments in the laboratory tests. Testing was done by treating specimens with WDCP's prior to exposure to the corrosive media and also by immersing specimens in the test media and then adding WDCP's to these solutions. Evaluation was by weight loss measurements and subsequent microscopic examination. In some of the tests, a novel method of estimating weight loss (during the course of a test) by analysis of small samples of solution was used. All six WDCP's tested were found to inhibit corrosion of the aluminium alloys significantly under the test conditions.

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